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Considerations in Applying Molecular Analysis of Different Fluids in a Condition Monitoring Program

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Abstract: Molecular analysis of oils by Fourier Transform Infrared (FT-IR) spectroscopy is becoming commonplace in condition monitoring programs. Providing a fast, direct measurement on species and properties of interest, molecular spectroscopy can supplement or replace other measurement techniques which are time consuming, or provide only an indirect measurement of the properties of interest. Molecular spectroscopy also offers other capabilities, such as calibration to classical physical tests, or the identification of an unknown fluid by searching against a spectral library of known fluids. Here, we will review some of the promises and pitfalls in molecular analysis for a condition monitoring program, with emphases on the general capabilities of molecular spectroscopy, and the amount of useful information (to a condition monitoring program) which can be generated when progressively less information is known about the machine being monitored.

Key Words: Condition monitoring; oil analysis; molecular spectroscopy; FT-IR, infrared; physical property test.

INTRODUCTION: Molecular analysis of new and used lubricating oils, hydraulic fluids, and fuels by Fourier Transform Infrared (FT-IR) spectroscopy is rapidly becoming commonplace in condition monitoring programs. Providing a fast, direct measurement on species and properties of interest, such as water, soot loading, coolant, oxidation, etc., FT-IR spectroscopy can supplement or replace other measurement techniques which are time consuming and generate additional wastes (such as Karl-Fisher titration for water and pentane insolubles for soot/dirt/carbon loading), or provide only an indirect measurement of the properties of interest (such as TAN/TBN/NN for oil breakdown and contamination). Infrared spectroscopy also offers other capabilities, such as calibration to classical physical tests (such as kinematic viscosity and TBN) by Principle Component Regression and Partial Least Squares (PCR/PLS), or the identification of an unknown fluid by searching against a spectral library of known fluids.

When applying molecular analysis in a condition monitoring program, the primary point to remember is that the information generated from the FT-IR spectrometer (or any other technique,

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for that matter) is to be used as a reliable, consistent source of information on the health of a system, not as an isolated exercise in pure analytical chemistry and instrumental analysis. One unfortunate misapplication of FT-IR spectroscopy in condition monitoring has been the use of spectral search (also called scan and search) to identify unknowns, and to attempt to use the search and identification results for condition monitoring purposes. As will be shown, this application will produce useful information only as long as nothing is wrong! Another desire in condition monitoring is to have the analyzer operate as much like a "black box" as possible, without the need for adjustments or modifications for the analysis of different fluid classes. An example of some instruments that approaches this ideal are the Arc and ICP spectrometers used for wear metal analysis. As these instruments can produce results for wear metal levels without knowledge or adjustment of the fluid characteristics, another unfortunate assumption is that any spectrometer, such as an FT-IR spectrometer, produces results in the same manner. However, even the Arc and ICP spectrometers do show a sample dependent response, and must be taken into account even more so when applying molecular analysis for condition monitoring. Finally, as many established condition monitoring programs which use the traditional physical property tests implement FT-IR spectroscopy, one "roadblock" they encounter is the desire for the results to be expressed in units and formats the maintenance personal are familiar, either for compatibility with their current expert system database or for simple "comfort". One way infrared spectroscopy can be quickly implemented in these programs is to use the power of Principle Component Regression / Partial Least Squares analysis (PCR/PLS), which can predict the physical response based on the infrared spectrum. PCR/PLS has been successfully used to generate predicted vacuum pentane insolubles, Total Base Number, and viscosity, in several condition monitoring programs. This allows the programs to begin implementation of the "newer" technology, reducing per-sample analysis costs, without forcing those who receive and act on the laboratory results into a sudden reeducation program.

AUTOMATIC SAMPLE IDENTIFICATION: Infrared spectroscopy has long been used in analytical chemistry for the identification of unknown compounds. As the infrared spectrum of each molecular species is unique, the identity of an unknown compound can be determined by comparison to a library of known compounds. These libraries were first distributed in large reference books, and later as compressed, computer searchable collections. The use of infrared spectroscopy in conjunction with easy-to-use search software and these library collections for unknown identification is one of the largest reasons FT-IR spectroscopy is so widely accepted in analytical laboratories.

As such capabilities are found in just about every modern infrared spectrometer, one application of infrared spectroscopy with search and identification has been to reduce the amount of paperwork and data entry in a condition monitoring program. In this application, it is assumed that the spectrometer can identify the type fluid from the infrared spectrum of the sample. From this identification, the system can then automatically determine the appropriate infrared analysis techniques to apply, and the condition alert or alarm limits, without the operator needing to keep track of the source of the sample and the characteristics of the machine. As noted above however, the objective is to provide useful information on the condition of a mechanical system, not a chemical analysis of submitted unknowns. Figure 1 shows the infrared spectrum of an unidentified fluid (top), and a small "library" of known fluids. While infrared spectroscopy can easily identify

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the fluid as a typical petroleum based crankcase lubricant, the real question to be answered is: "is this machine operating within normal limits?"
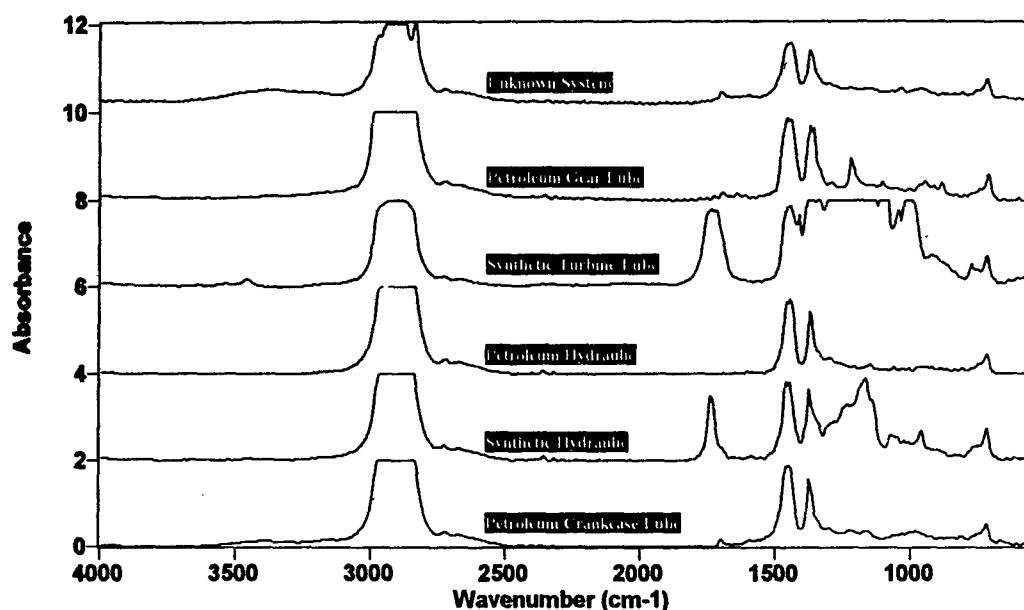

Figure 1. Does the fluid from the "Unknown System" (top) indicate that the machine being monitored is functioning within limits?

In this case, the correct answer can not be determined. While the spectrometer and software can identify the fluid as most similar to a petroleum crankcase lubricant, the analysis information would only be useful if the sample actually came from an engine crankcase. The obvious failure of the search and identification approach is the inability to alert the operators when the wrong fluid is used in a machine. While this may be an uncommon mistake in the real world, even one occurrence may place the component in unacceptable risk, not to mention the total system, productivity, associated property, and lives. A more common example is the case where an engine crankcase oil sample is correctly determined to be a petroleum crankcase, and the soot or dirt level is determined by the absorbance at 2000 cm^{-1} (Figure 2). Once again, the question is not "what is the soot/dirt/carbon level", but "is this machine operating within normal and acceptable soot/dirt/carbon levels?" Once again, without knowing if this sample came from a diesel engine, gasoline engine, or a natural gas engine, the answer can not be determined. Diagnosis of the condition of a machine can not be made when the requirements and characteristics of the machine are unknown.
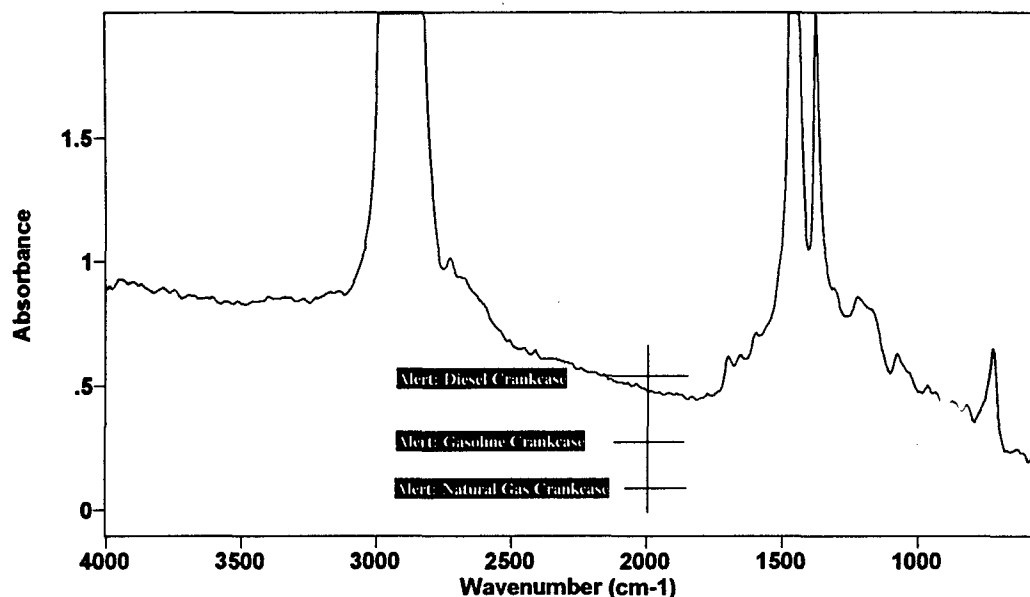
Figure 2. Does this engine have an excessive soot loading?

THE "BLACK BOX" APPROACH: The ideal analytical instrument operates without any user input or interaction, and produces accurate, informative results irrespective of the conditions of use, knowledge of the sample, source of the sample, chemistry of the system, or information from other sources. Part of this has been visited above. One example of some instruments that approach this ideal are the Arc and ICP atomic emission spectrometers used for wear metal analysis. While at first it may seem that these instruments produce informative results irrespective of the sample, in fact these instruments used in condition monitoring programs have been typically optimized for the analysis of th lubricants. Thus, much of the information and knowledge of the samples analyzed has already been built into the hardware and software of these instruments.

Not even atomic emission spectrometers provide accurate measurements of wear metals in lubricants. Because of the different energy characteristics of the excitation sources in arc and ICP spectrometers, different emission lines may be used for some elements. Thus, measurement of a given metal may be performed using different emission lines with different relative intensities. Arc and ICP spectrometers correct this variation, as well as producing results in concentration units, by calibration with organometallic compounds dissolved in a base oil matrix. Even with calibration, the characteristics of sample introduction to these different instruments will produce different results. The nebulizer and plasma on the ICP spectrometers are unable to generate a signal from particles less than 3 microns in size, as compared to emission signals which can be generated from particles 10 microns and possible larger from arc spectrometers. [1] Thus, for the same lubricant sample with wear metal particles the two different types of spectrometers will

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produce different results for wear metal levels. These two different instruments are useful in condition monitoring programs because most condition monitoring programs trend the wear metal levels from on type of instrument, or in essence, the spectrometers are always measuring one consistent, well defined matrix: a high temperature plasma.

Molecular spectroscopy can also achieve this "black box" level, if as noted in the last sentence above, a single, well defined matrix is measured by the FT-IR spectrometer. However, many condition monitoring programs perform analysis on a wide range of fluids from different systems, and thus different samples constitute a different matrix measured by the spectrometer. Previous work has demonstrated the differences in response in the infrared absorbance of water in two different types of lubricants: petroleum based crankcase lubricants and synthetic turbine lubricants. [2] Figure 3 shows the difference in the hydrogen bonded OH (water) absorbance region for the same amount of water in a typical petroleum based crankcase lubricant and
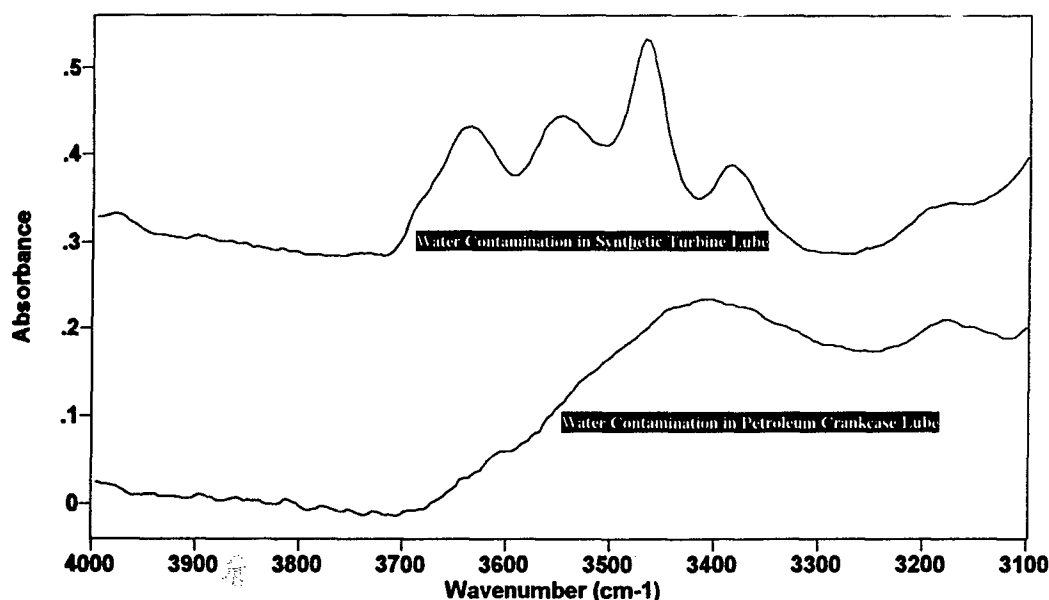

Figure 3. Water contamination at 2500 ppm in petroleum based lube (bottom) and a polyol ester based lube (top).

a polyol ester based synthetic turbine lubricant. As can be seen, there are significant differences in the water response between the petroleum based lubricant and the synthetic based lubricant, mostly due to differences in hydrogen bonding between the water and the lubricant and additive package. Assuming that water will give the same response independent of the matrix in which it exists clearly will lead to erroneous results.

A common technique for observing individual components in a strongly absorbing matrix is to use computer spectral subtraction, which produces spectral results that are similar to using a pair of matched cells on an old scanning double-beam spectrophotometer. Spectral subtraction is then used to remove the spectral response of the base oil, with the assumption that this mathematical technique removes the interactions from the base matrix (the oil) with the sample response (component of interest), and thus the same quantitative analysis methods and calibrations can be used independent of the class of lubricant. [3] Figure 4 shows the danger of
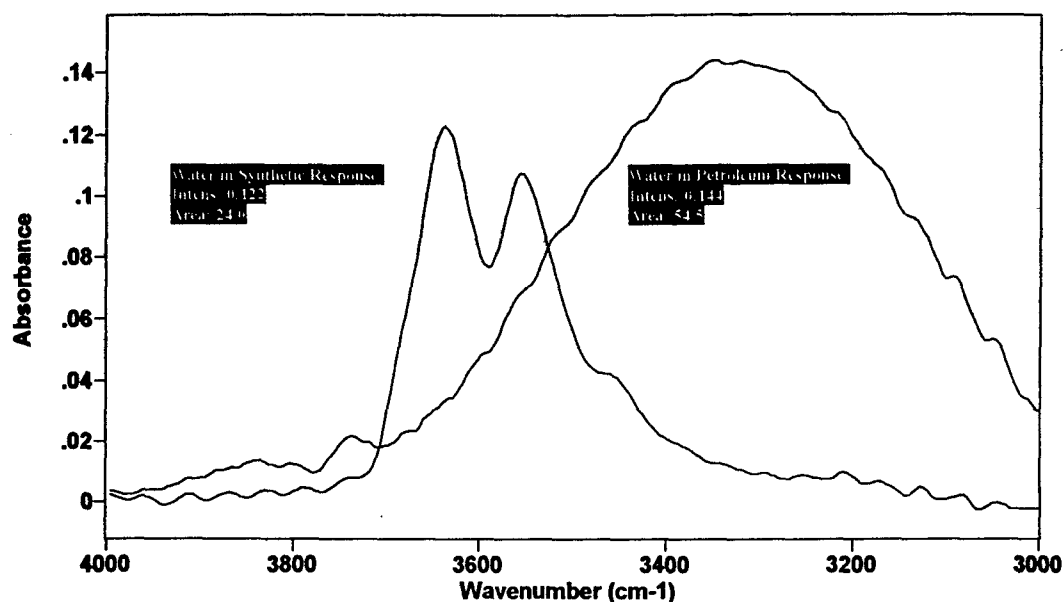

Figure 4. New oil subtracted spectra, each with 1000 ppm water.

this assumption. Both lubricants, a typical petroleum crankcase lubricant and a polyol ester synthetic (Mil-L-23699) were spiked with 1000 ppm of water, and then the new reference oil subtracted. Classical infrared quantitative analysis relates either the intensity of the band or the area under the band to the component concentration. As can be seen on the figure, a calibration based on an intensity / concentration correlation for water will result in a nearly 20% error, and a calibration based on the area under the curve using water in petroleum standards will be in error by 50%! While it is possible to set up instrument such that it produces a number no matter what type of sample it is presented, one should be wary of such an analysis technique without further investigation.

ADVANCED QUANTITATIVE ANALYSIS: While molecular analysis using infrared spectroscopy offers great promise in condition monitoring programs, there is always reluctance to employ new analytical methods because of either the familiarity of the old methods, machinery supplier guidelines and recommendations, or because the various maintenance rules and

guidelines, either human interpreted or as dictated by an expert system, require results from the old methods. Many of these tests for molecular species of interest are based on what is generally referred to as physical property tests, where a physical measurement of the lubricant is related to a machine condition or recommended action. These tests usually involve "wet" chemical sample preparation and analysis, such as measuring the soot or carbon loading by diluting a sample of used oil with pentane, filtering or centrifuging the solids out, weighing the separated solids, and then calculating the percent solids in the oil. While infrared spectroscopy can measure the amount of soot based on the amount of baseline offset and tilt due to scattering of the suspended particles, one limitation is that such a measurement is affected by both the concentration of the suspended soot and the average particle size and distribution, making a classical infrared correlation to percent insolubles difficult. [4]

Besides the classical infrared quantitative analysis tools, relating the intensity or area of a single band to the desired property, statisticians have created a wide range of advanced interpretation and analysis tools such as Principle Component Regression and Partial Least Squares (PCR/PLS) analysis. Rather than "reducing" a single band in the infrared spectrum to a single number based on the intensity or area, PCR/PLS analysis tools use the entire "profile" of the infrared spectrum, and with a sufficient training set of spectra, can often create surprising correlations between the infrared response and a desired physical property. One example of this was recently encountered at CSX laboratories, where the infrared soot measurements from a smaller set of EMD engines
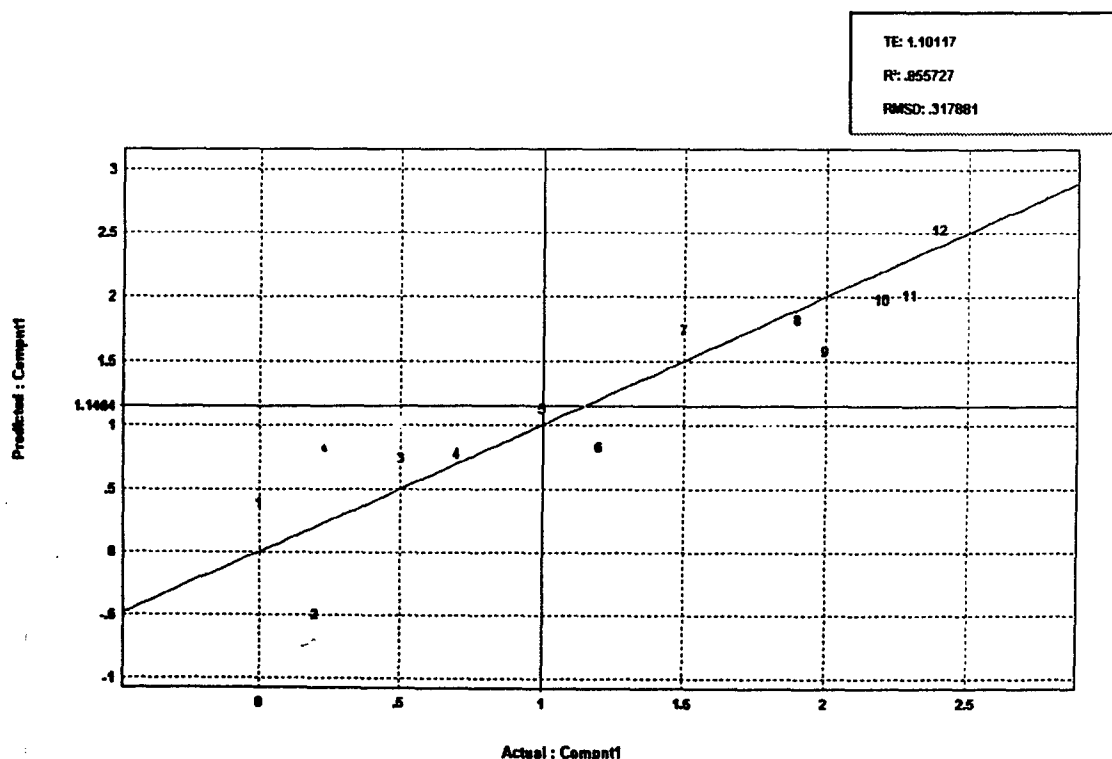

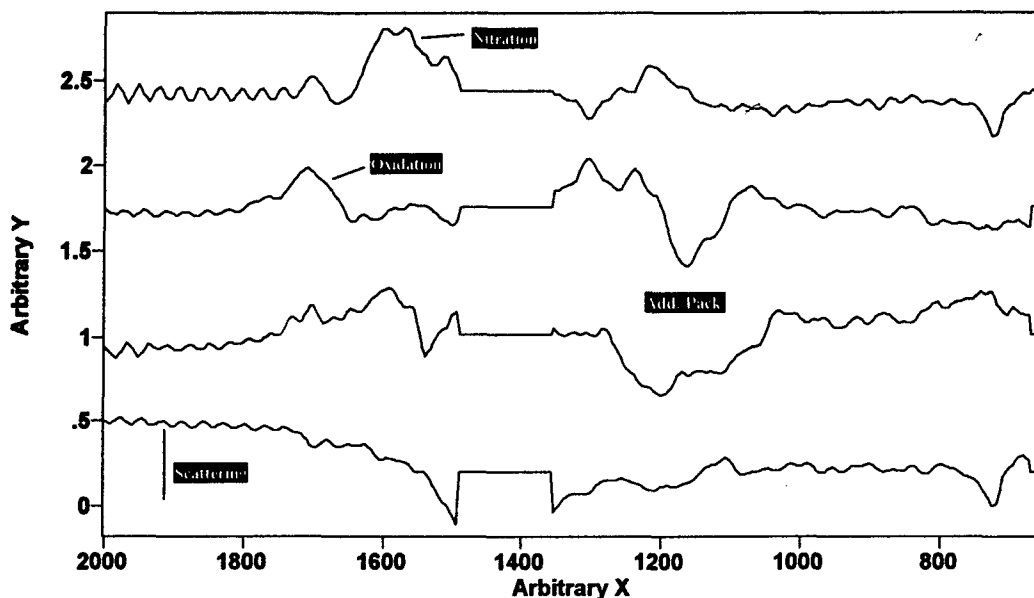Figure 5. PCR/PLS correlation for vacuum pentane insolubles.

Figure 6. Principle component spectral factors influencing vacuum pentane insolubles measurement.

did not correlate to the infrared soot measurements from the GE engines. This too was traced back to average particle size and distribution differences, as the EMD and GE engines used different filters with different pore sizes. The PCR/PLS analysis tools were able to generate an acceptable correlation to their vacuum pentane insolubles test (Vac. P.I.), to within +/- 0.5% (figure 5), as compared to the wet chemical method reproducibility of +/- 0.2 % across the range. While of lower precision, the savings in manpower and solvent usage / disposal more than justified the change. The PCR/PLS also allows an examination of some of the molecular level components and interactions which are related to the physical property of interest. In figure 6, some of the principle component spectra generated from a PCR/PLS analysis of used samples from 62 EMD engines, covering the range of Vac. P.I. readings, are displayed. From inspection of the spectra, some molecular level correlations and influences can be determined. For example, the first component (bottom spectrum in the figure) shows the classical baseline offset and tilt due to the scattering from the soot particles. However, the PCR/PLS analysis uses not only this factor, but some of the other factors plotted above. The second spectra (factors) from the bottom show a correlation between the additive package and the vacuum pentane insolubles measurement, while the third and fourth spectra (factors) show a correlation between the oxidation and nitration to the Vac. P.I. response. Both of these correlations become obvious when one reflects that the Vac. P.I. levels will increase as the additive package components, especially the detergents and dispersents, decrease, and the Vac. P.I. levels will increase with the age of the oil charge, which will also show an increase in the oxidation and nitration due to age and use. The PCR/PLS

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correlation uses the above calculated factors, along several other factors not displayed, to produce a predicted Vac. P.I. sufficient for the maintenance needs.

While generating a correlation to the pentane insolubles was shown to be feasible, other classical wet chemical techniques may give one pause. One example of this is the Total Base Number (TBN) titration, which is used to measure the amount of acid species in an oil, with the assumption that the acid species are due to oxidative breakdown of the oil. The sample is titrated to an end point, and the actual measurement is expressed as milliequivalents of potassium hydroxide per gram of sample. While acid generated species from oil breakdown are measured, there are a considerable number of possible internal or external species which can also give rise to acid species. In fact, while ASTM method D 5372 notes the use of this titration test, it also notes that "the use of infrared analysis may serve as a more reliable method for detection of oxidation". [5] In this case however, the laboratory and data system management needs dictated
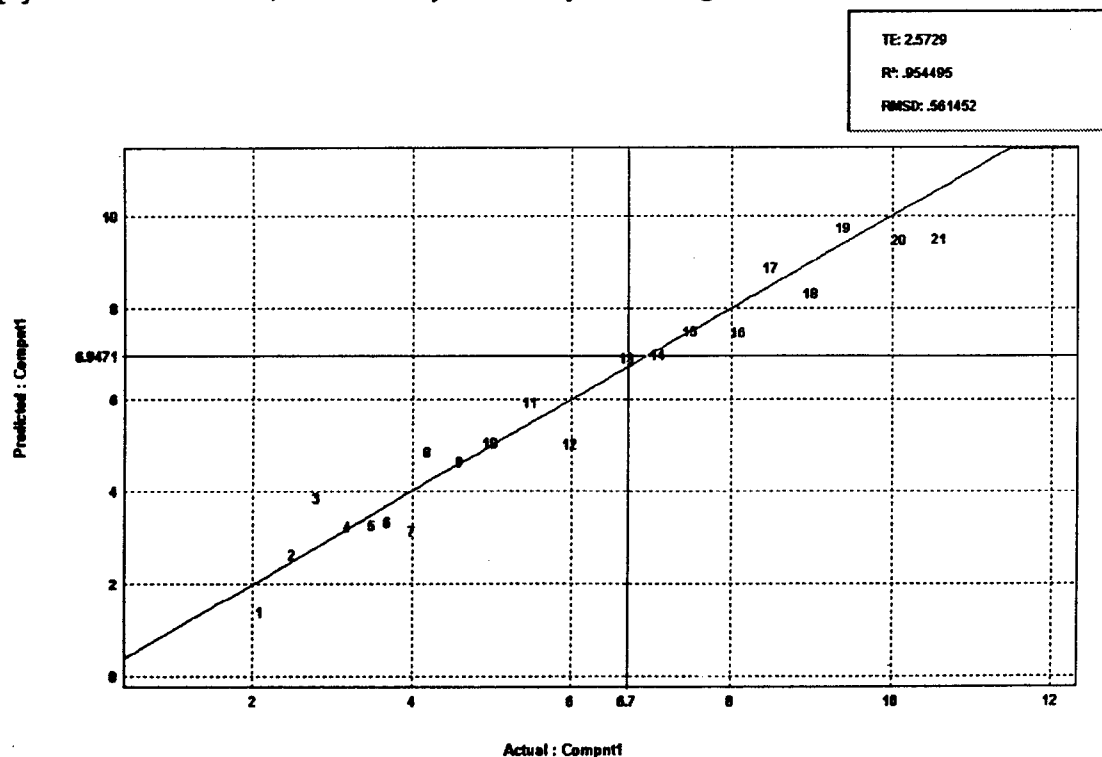

Figure 6. PCR/PLS correlation to TBN

that the new system continue to produce TBN measurements for ensured compatibility with current procedures. Here, PCR/PLS analysis once again produced an acceptable correlation with the desired physical property (Figure 6).

In both these cases however, note that the typical fluids analyzed represented a very narrow range of all possible lubricants which may be encountered in a large condition monitoring program. All the above sites used a relatively restricted range of lubricants, typically specifying both base oil characteristics and a particular additive package blended at a specific level, and thus the number

of variances that the PCR/PLS analysis tools had to account were relatively limited. In an independent, commercial condition monitoring laboratory, where a much larger range of petroleum based lubricants are used, the size of the training set must be increased to account for the additional variances. While PCR/PLS analysis offers the promise of correlating the infrared spectrum to many physical properties of interest, anyone embarking on this path should be aware that these tools can only accurately predict characteristics in an unknown if it has "seen" that type of unknown previously. As in the above example of applying the calibration of water in a petroleum based lubricant to the analysis of a synthetic lubricant will lead to errors, similar misapplication of advanced analysis tools will produce similar misinformation.

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